# Lawrence Berkeley National Laboratory

(University of California, University of California)

# Identifying semiconductors by d.c. ionization conductivity

# Identifying semiconductors by d.c. ionization conductivity

## Abstract

We describe a method for identifying semiconductor radiation detector materials based on the mobility of internally generated electrons and holes. It was designed for the early stages of exploration, when samples are not available as single crystals, but as crystalline powders. Samples are confined under pressure in an electric field and the increase in current resulting from exposure to a high-intensity source of 60Co gamma rays (i.e. the ionization current) is measured. We find that for known semiconductors the d.c. ionization current depends on voltage according to the Hecht equation, and for known insulators the d.c. ionization current is below our detection limits. This shows that the method can identify semiconductors in spite of significant carrier trapping. Using this method, we have determined that BiOI, PbIF, BiPbO2Cl, BiPbO2Br, BiPbO2I, Bi2GdO4Cl, Pb3O2I2, and Pb5O4I2 are semiconductors.

# Identifying Semiconductors
# by D.C. Ionization Conductivity

Stephen E. Derenzo, *Fellow, IEEE*, Edith Bourret-Courchesne, Floyd J. James,
Mattias K. Klintenberg, Yetta Porter-Chapman, Jie Wang, and Marvin J. Weber

*Abstract*–**We describe a method for identifying semiconductor radiation detector materials based on the mobility of internally generated electrons and holes. It was designed for the early stages of exploration, when samples are not available as single crystals, but as crystalline powders. Samples are confined under pressure in an electric field and the increase in current resulting from exposure to a high-intensity source of $^{60}$Co gamma rays (i.e. the ionization current) is measured. We find that for known semiconductors the d.c. ionization current depends on voltage according to the Hecht equation, and for known insulators the d.c. ionization current is below our detection limits. This shows that the method can identify semiconductors in spite of significant carrier trapping. Using this method, we have determined that BiOI, PbIF, BiPbO$_2$Cl, BiPbO$_2$Br, BiPbO$_2$I, Bi$_2$GdO$_4$Cl, Pb$_3$O$_2$I$_2$, and Pb$_5$O$_4$I$_2$ are semiconductors.**

## I. INTRODUCTION

A successful semiconductor radiation detector material should have good stopping power, can be obtained as large crystals at low cost, have acceptable carrier mobilities and lifetimes, and operate at ambient temperatures. Despite the fact that available detector materials fall short of these goals, the list of candidate materials has not grown substantially during the past 25 years [1-3]. Motivated by the possibility that better semiconductor detector materials can be found among the thousands of known but unexplored crystal forms [4, 5], we have developed a method for identifying them during the early stages of exploration, when samples are not available as single crystals, but as crystalline powders.

Because the defining characteristic of a semiconductor radiation detector material is the mobility of internally generated electron and hole charge carriers, we have developed an apparatus for confining a powder sample under pressure in an electric field and measuring the d.c. current induced by a high-intensity $^{60}$Co gamma ray source. For known semiconductors we find that this current is consistent with the generation and transport of electron and hole carriers with a voltage-independent mobility-lifetime product characteristic of semiconductors. No such current was observed for known insulators, consistent with carrier self trapping.

New semiconductor materials are candidates not only for radiation detectors that detect charge carriers externally but also for scintillators that exhibit ultra-fast ($\approx$1 ns) radiative recombination [6, 7].

The value of the band gap alone is not useful for identifying semiconductors because some (e.g. diamond) have a high band gap. A temperature-dependent electrical conductivity is not useful because it is negligible in undoped semiconductors with band gaps above 1.5 eV but can be large for insulators that exhibit ionic conductivity. For example NaCl is not a semiconductor because holes are spontaneously trapped on the Cl$_2^-$ V$_k$ center but the electrical conductivity is high due to motion of the Cl$^-$ ions.

## II. BACKGROUND

In a semiconductor, the current resulting from the internal generation of electrons and holes in an electric field is described by the Hecht equation [8]:

$$I = I_0 \left[ d' / d \right] \left[ 1 - \exp(-d / d') \right]$$

where $I_0$ is the rate of electron-hole production and $d$ is the sample thickness. The average drift distance before trapping and recombination is given by $d' = \mu\tau E$, where $\mu$ and $\tau$ are the carrier mobility and lifetime, respectively, and E is the electric field strength. Detrapping and retrapping may occur, but this only adds to the effective carrier lifetime $\tau$. In a crystalline semiconductor powder there is significant trapping on the particle surfaces, most of the carriers recombine in the material, $d' << d$, and the equation reduces to

$$I = I_0 d' / d = I_0 \mu\tau V / d^2$$

where $V$ is the applied voltage.

However, if even one carrier type is self trapped, the other carrier is bound to the first by Coulomb attraction, and $d'$ and $I$ are essentially zero. Such materials are true insulators. Note

that the photoconductivity observed in insulators is measured as an a.c. current of electrons in the conduction band and would not appear in our steady-state d.c. measurements.

Spontaneous self trapping of carriers is known to occur in many crystals. One well-known example is the spontaneous trapping of holes by lattice relaxation to form $V_k$ centers in alkali halides. It has been pointed out that carrier self trapping occurs if the charge localization energy is less than the lattice relaxation energy [9]. First-principles calculations capable of predicting self trapping in the general case have yet to be developed. Specifically, the inability of Density Functional Theory to describe localized charge states and the inability of Hartree-Falk Theory to describe delocalized charge states is reviewed in ref [10].

## III. METHODS AND PROCEDURES

Figure 1 shows our apparatus for confining a powder sample between two titanium anvils, 3 mm in diameter, in an electric field. The design is based on that of Wang and Sleight who showed that a pressure of 0.5 N/mm$^2$ is sufficient to provide a continuous electrical path through a powder sample of n-type ZnO [11]. In this work a guard ring has been added so that the ammeter records only current that passes through the sample and not the current that passes though the air. Current passing through the Delrin is less than 10 pA.
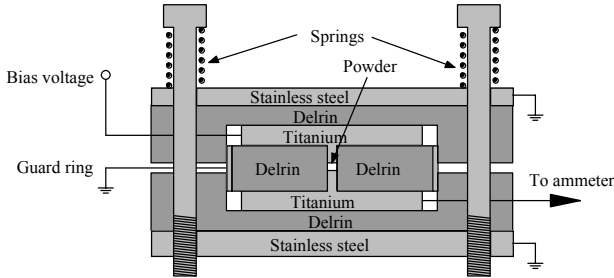


Fig. 1. Cutaway sketch of the cylindrical pressure cell used for measuring the d.c. electrical conductivity of compressed powders. The powder sample is placed in the central region between 3 mm diameter titanium electrical contacts and subjected to a pressure of 0.5 N/mm$^2$.

The samples used were either the highest purity materials obtained from chemical suppliers or synthesized in our laboratory from highest purity available starting materials. For all samples the crystal phase was checked by x-ray diffraction and a weighed amount was used to produce a compressed thickness of approximately 1 mm (volume 7 mm$^3$).

After a powder sample is pressed between the titanium anvils, the electrical conductivity is measured for a range of applied voltages (source off) and then the measurements are repeated during irradiation by 1.2 MeV Co-60 gamma rays from a 450 Ci cancer therapy unit (source on). The dose rate was 1,500 rad/min. The currents were measured using a Keithley model 617 electrometer.

## IV. RESULTS

Figure 2 shows the current vs. time for BiPbO$_2$Cl at voltages of 2 V (a) and 100 V (b). After the voltage is applied the material polarizes and reaches a steady current. When the source is turned on traps fill and the current increases to an equilibrium level. At this point the rate of generation of electron-hole pairs is equal to the rate of trapping and recombination. When the source is removed the current drops to the initial level as the carriers detrap.
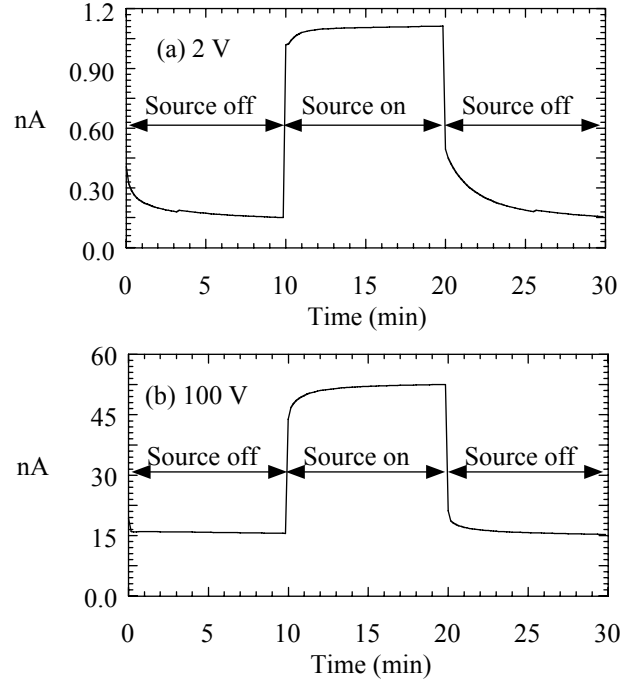


Figure 2. Plot of current vs. time for BiPbO$_2$Cl at (a) 2 V and at (b) 100 V. See text for details.

Figure 3 shows the d.c. ionization currents (i.e. source on minus source off) for seven known semiconductors ZnTe, ZnO, GaAs, CdS, HgI$_2$, PbI$_2$, and diamond as a function of applied voltage. All currents reported here are steady state values. The relationship between ionization current and voltage is nearly linear as expected from the Hecht equation for the case where $d' << d$.

Variations between samples are due to differences in $\mu\tau$ products. Since most of the trapping is on the microcrystal surfaces, the observed current values are not indicative of what would be collected from single crystals.

Tables I and II list the density, experimentally measured band gap and currents I(off) and I(on) measured at 100 V with the source off and on, respectively for the materials studied in this work. Band gaps were taken from ref [12] or were determined in our laboratory from measurements of reflectance vs. wavelength. While hole hopping is known to occur for CsI [13], the resulting current is well below those in Table II.

Table I lists materials whose ionization current is too small to be identified as semiconductors. Table II lists materials

whose ionization current increases with voltage and can be identified as semiconductors. In Table II many materials exhibit significant I(off) values due to ionic conduction and n- or p-type doping. The large currents seen for the semiconductors ZnO and ZnTe are due to the latter.

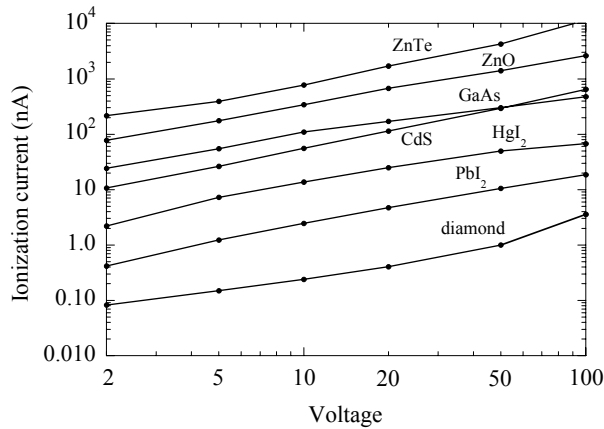| | | | | |
|---|---|---|---|---|
| ZnS | 4.1 | 3.8 | 5.07 | 5.59 |
| ZnTe | 5.8 | 2.3 | 482,000 | 493,000 |

* New determination as semiconductors
a Current at 100 V with source off
b Current at 100 V with source on

Figure 4 shows the ionization current for diamond, BiOF, $Lu_2SiO_5$, $Bi_2SiO_5$, and $SiO_2$. Although the diamond powder has significant carrier trapping, it exhibits an ionization current that rises with applied voltage, while the others show no measurable ionization currents for all voltages measured. The ionization currents for $Bi_4Ge_3O_{12}$, CsI, and $PbF_2$ are also consistent with zero over the same range of voltages.



Figure 3. Plot of ionization current [I(on) − I(off)] vs. applied voltage for seven known semiconductor powders measured in this work. Experimental uncertainties in current are approximately 10% + 0.02 nA.

TABLE I
MATERIALS NOT IDENTIFIED AS SEMICONDUCTORS

| Compound | $\rho$ (gm/cm$^3$) | $E_G$ (eV) | I(off)$^a$ (nA) | I(on)$^b$ (nA) |
|---|---|---|---|---|
| $Bi_4Ge_3O_{12}$ | 7.1 | 4.2 | 2.50 | 2.51 |
| $Bi_2SiO_5$ | 7.9 | | 0.14 | 0.16 |
| BiOF | 9.2 | | 74.7 | 74.6 |
| CsI | 4.7 | 6.2 | 0.58 | 0.67 |
| $Lu_2SiO_5$ | 7.4 | 6.4 | 1.43 | 1.40 |
| $PbBr_2$ | 6.7 | 3.2 | 1097 | 1093 |
| $PbCl_2$ | 5.9 | 3.9 | 113 | 110 |
| $PbF_2$ | 7.8 | 5.0 | 1150 | 1151 |
| $SiO_2$ | 2.6 | 8.4 | 1.01 | 1.02 |

TABLE II
MATERIALS IDENTIFIED AS SEMICONDUCTORS

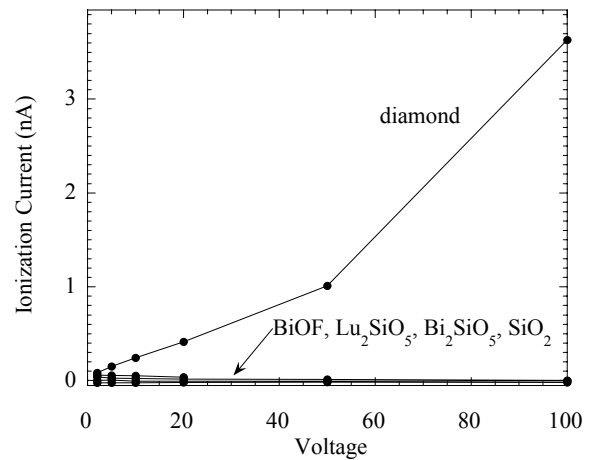| Compound | $\rho$ (gm/cm$^3$) | $E_G$ (eV) | I(off)$^a$ (nA) | I(on)$^b$ (nA) |
|---|---|---|---|---|
| *$BiGdO_4Cl$ | 8.4 | 2.7 | 733 | 904 |
| *$BiPbO_2Cl$ | 8.3 | 2.7 | 14.3 | 52.7 |
| *$BiPbO_2Br$ | 8.6 | 2.8 | 17.5 | 25.3 |
| *$BiPbO_2I$ | 8.6 | 2.7 | 6.1 | 703 |
| *BiOI | 8.1 | 2.1 | 1.80 | 4.11 |
| CdS | 4.8 | 2.5 | 4.9 | 650 |
| diamond | 3.5 | 5.4 | 0.04 | 3.6 |
| GaAs | 5.3 | 1.5 | 1417 | 1894 |
| $HgI_2$ | 6.4 | 2.2 | 10.4 | 78 |
| *$Pb_3O_2I_2$ | 7.6 | 2.7 | 2.5 | 27 |
| *$Pb_5O_4I_2$ | | 2.7 | 0.81 | 1.24 |
| *PbFI | 7.4 | 3.0 | 5.5 | 9.3 |
| $PbI_2$ | 6.1 | 2.5 | 4.0 | 22.6 |
| PbO | 9.6 | 2.7 | 0.31 | 2.37 |
| ZnO | 5.7 | 3.4 | 10,500 | 13,100 |



Figure 4. Ionization current [I(on) − I(off)] vs. voltage. The ionization current increases with voltage for the known semiconductor diamond but remains low at all voltages for BiOF, $Lu_2SiO_5$, $Bi_2SiO_5$, and $SiO_2$.

Figure 5 shows a plot of ionization current vs. applied voltage for $PbBiO_2Cl$, $PbBiO_2Br$, $PbBiO_2I$, $Bi_2GdO_4Cl$, BiOI, PbIF, $Pb_3O_2I_2$, and $Pb_5O_4I_2$, identifying them as semiconductors. Because this method uses the difference between the source on and source off conditions, it cannot be used for samples whose ionic conductivity is much larger than the ionization conductivity.
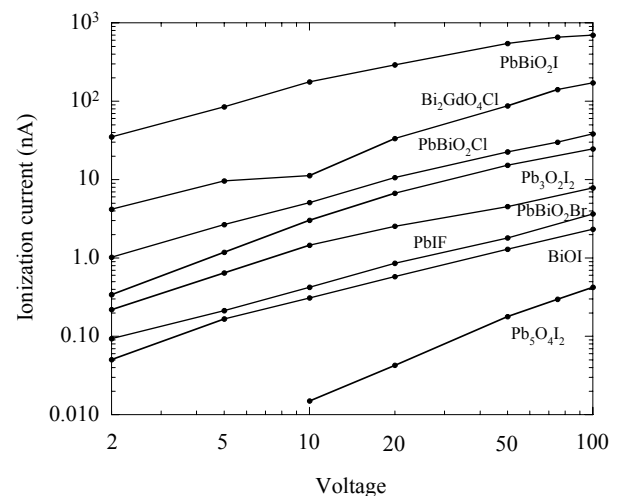
Figure 5. Plot of ionization current [I(on) – I(off)] vs. applied voltage for six semiconductors identified in this work. Experimental uncertainties in current are approximately 10% + 0.02 nA.

## V. DISCUSSION

In modern usage, semiconductor materials (circuit elements and nuclear detectors) are valued for their ability to conduct internal electrons and holes over macroscopic distances. We find that it is possible to determine experimentally which materials have this property by measuring the change in their electrical conductivity during exposure to ionizing radiation. In accord with this and the notion that all pure inorganic materials in a specific crystal structure can be classified as either metals, semiconductors or insulators, we suggest defining a semiconductor as "a non-metallic solid in which electrons and holes are mobile," and an insulator as "a solid in which electrons or holes are self trapped." Unlike semiconductors, metals have partially filled valence bands and are electrically conductive at temperatures approaching 0K. Furthermore, we suggest that the common definitions of the semiconductor as "a material that is neither a good electrical conductor or a good electrical insulator" or as "a material whose electrical conductivity can be changed by temperature or by doping" do not reflect the processes of either ionic conduction or of carrier transport and self trapping, and are not useful in identifying semiconductors experimentally.

## VI. CONCLUSIONS

Despite significant trapping on microcrystal surfaces, semiconductors can be identified in compressed powder form by an increase in d.c. conductivity during exposure to ionizing radiation in accordance with the Hecht equation. In known insulators, no increase in d.c. conductivity was measured during exposure to ionizing radiation. Using this method we have identified eight heavy-atom semiconductors: BiOI, PbIF, $BiPbO_2Cl$, $BiPbO_2Br$, $BiPbO_2I$, $Bi_2GdO_4Cl$, $Pb_3O_2I_2$, and $Pb_5O_4I_2$. All of these have densities exceeding 7 and are worthy of further exploration in single crystal form as radiation detector materials.

## REFERENCES

[1] G. Armantrout, S. Swierkowski, J. Sherohman, et al., "What can be expected from high-Z semiconductor detectors?," IEEE Trans Nucl Sci, vol. NS-24, pp. 121-125, 1977.

[2] C. Manfredotti, R. Murri, A. Quirini, et al., "$PbI_2$ as a nuclear particle detector," IEEE Trans Nucl Sci, vol. NS-24, pp. 126-128, 1977.

[3] K. S. Shah, J. C. Lund, F. Olschner, et al., "Thallium bromide radiation detectors," IEEE Trans Nucl Sci, vol. NS-36, pp. 199-202, 1989.

[4] "Inorganic Crystal Structure Database, Fachinformationszentrum Karlsruhe, Germany" 2005.

[5] "Powder Diffraction File, International Center for Diffraction Data, Newtown Square, PA, U.S.A." 2005.

[6] S. E. Derenzo, M. J. Weber and M. K. Klintenberg, "Temperature dependence of the fast, near-band-edge scintillation from CuI, $HgI_2$, $PbI_2$, ZnO:Ga, and CdS:In," Nucl Instr Meth, vol. A486, pp. 214-219, 2002.

[7] S. E. Derenzo, E. Bourret-Courchesne, M. J. Weber, et al., "Scintillation studies of CdS(In): effects of codoping strategies," Nucl Instr Meth, vol. A537, pp. 261-265, 2005.

[8] K. Hecht, "Zum Mechanismus des lichtelektrischen Primärstromes in isolierenden Kristallen," Zeitschrift fur Physik (Berlin), vol. 77, pp. 235, 1932.

[9] K. S. Song and R. T. Williams, "Self-Trapped Excitons, 2nd edition," pp. 404, Springer-Verlag, New York, 1996.

[10] J. L. Gavartin, P. V. Sushko and A. L. Shluger, "Modeling charge self-trapping in wide-gap dielectrics: localization problem in local density functionals," Phys Rev B, vol. 67, pp. 035108-8, 2003.

[11] R. Wang, A. Sleight and D. Cleary, "High conductivity in gallium-doped zinc oxide powders," Chem Mater, vol. 8, pp. 433-439, 1996.

[12] W. H. Strehlow and E. L. Cook, "Compilation of energy band gaps in elemental and binary compound semiconductors and insulators," J Phys Chem Ref Data, vol. 2, pp. 163- 199, 1973.

[13] J. D. Valentine, W. W. Moses, S. E. Derenzo, et al., "Temperature dependence of CsI(Tl) gamma-ray scintillation decay time constants and emission spectrum," Nucl Instr Meth, vol. A325, pp. 147-157, 1993.